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# Antisite-Defect-Induced Surface Segregation in Ordered NiPt Alloy

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By means of first principles simulations we demonstrate that tiny deviations from stoichiometry in the bulk composition of the NiPt- $L1_0$  ordered alloy have a great impact on the atomic configuration of the (111) surface. We predict that at  $T = 600$  K the (111) surface of the  $\text{Ni}_{51}\text{Pt}_{49}$  and  $\text{Ni}_{50}\text{Pt}_{50}$  alloys corresponds to the (111) truncation of the bulk  $L1_0$  ordered structure. However, the (111) surface of the nickel deficient  $\text{Ni}_{49}\text{Pt}_{51}$  alloy is strongly enriched by Pt and should exhibit the pattern of the  $2 \times 2$  structure. Such a drastic change in the segregation behavior is due to the presence of different antisite defects in the Ni- and Pt-rich alloys and is a manifestation of the so-called off-stoichiometric effect.

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Surface segregation phenomenon, which was predicted by Gibbs at the turn of the XIX century, has today become of great scientific and technological importance. Its experimental investigation started about three decades ago with the development of the surface sensitive techniques [1,2]. A substantial amount of work, both theoretically and experimentally, has been devoted to the investigation of surface segregation in random metallic alloys. Also in ordered alloys the surface composition might exhibit quite complicated behavior as a function of the bulk alloy internal parameters but also on external or experimental conditions [3]. There are several basic reasons for the existence of such a complicated behavior. First of all, most facets of ordered alloys have quite complicated structures which are not unique due to the existence of several possible truncations and have a composition different from the ideal stoichiometry. At the same time a realization of a particular surface structure may be determined by purely kinetic processes, which, for instance, seems to be the case for some oxides and carbides [4]. Another factor is the competition between atomic ordering effects on the underlying lattice and a tendency of alloy components to segregate towards particular layers or specific positions. Even in random metallic alloys, at temperatures above the order-disorder phase transition, such a competition may lead to unusual effects, such as the orientation dependence of surface segregations in NiPt alloys, observed experimentally in Refs. [5,6] and explained theoretically in Refs. [7,8].

The role of the ordering effects at the surface significantly increases below the order-disorder phase transition. In random alloys the surface segregation increases monotonously with decreasing temperature. However, if the ordering energy is greater than the corresponding values of the surface segregation energies in an ordered alloy, the temperature dependence of the surface segregation will exhibit so-called “endothermic” behavior,

where the segregation level *decreases* with decreasing temperature [9,10]. At the same time, the order at the surface itself may be significantly hampered compared to the corresponding layers in the bulk due to a frustration of the ordering at the surface which leads to the so-called surface induced disorder [11,12].

Despite all the complications due to atomic ordering, it is generally believed that the major factors which govern the surface segregation in the case of ordered alloys are the crystal structure, surface orientation, and competition between ordering and surface segregation. In this Letter we demonstrate, however, that there is another important factor, the bulk alloy composition, which may determine the equilibrium surface composition and configuration. In random alloys the surface segregation is a smooth function of the bulk alloy composition. This situation should change dramatically in the case of ordered alloys, and the reason is that a deviation from the stoichiometric composition leads to the appearance of specific constitutional defects (either antisites or vacancies or some combination of them), which are different on the different sides of the stoichiometric composition.

From a general formalism one finds that this immediately leads to the appearance of a certain jump in the chemical potential of the alloy components at the stoichiometric composition of ordered alloys [13–15]. Although such a jump has no consequences for the point defect structures of the ordered alloys at a fixed alloy composition (which is the usual experimental situation) [16], it becomes important in the case of extended defects such as dislocations and surfaces, where the bulk defect structure may dramatically affect, for instance, the dislocation dissociation reaction [17] or initial stages of the surface oxidation [18]. Correspondingly it may also have great impact on the surface segregation [19]. By means of *ab initio* simulations, we show in the present paper that the so-called off-stoichiometric effect [19] can take place

in a real system, and we investigate the temperature dependence of the surface concentration profiles below and above the bulk order-disorder phase transition.

In contrast to practically all the previous Monte Carlo (MC) simulations for the configurational thermodynamics of the surfaces of ordered alloys which have been done on the basis of model interactions, we will consider a real system, the (111) surface of  $\text{Ni}_{50}\text{Pt}_{50}$ . This alloy exhibits moderate ordering and undergoes a phase transition from a disordered phase to the  $L1_0$  ordered phase in the range of concentration 40–55 at. % Pt [20] at temperatures 800–920 K. The (111) surface has only one possible truncation with a  $(2 \times 1)$  structure represented by a stack of alternating  $\langle 110 \rangle$  rows of Ni and Pt atoms, and thus it has the bulk stoichiometric composition in the completely ordered state. This surface is also interesting since it may exhibit both the surface induced disorder [12] and endothermic segregation.

There are different ways to obtain the corresponding effective interactions which enter the configurational Hamiltonian in the Monte Carlo method by means of the first-principles electronic theory [21]. We have used the total energy calculations and the numerically efficient screened generalized perturbation method [22,23] in the framework of the bulk and surface Korringa-Kohn-Rostoker Green's function method in the atomic sphere approximation with multiple moment correction to the Madelung energy ( $\text{ASA} + M$ ) and the coherent potential approximation [24,25]. The calculated effective interactions for the (111) surface of  $\text{Ni}_{50}\text{Pt}_{50}$  used in this work are presented and analyzed in Ref. [8]. The local relaxations have been taken into account in the effective tetrahedron volume approach [8] while possible surface specific lattice relaxations are not included. However, since the  $L1_0(111)$  surface is close packed, such relaxations are expected to be small. The complete computational scheme has already been successfully applied for the investigations of surface segregations in random NiPt alloys at (111) and (110) surfaces at temperatures above the order-disorder transition temperature [8].

Bulk MC calculations have been performed in the temperature interval of 600–1400 K and the calculated bulk order-disorder transition temperature  $T_c = 1050$  K of the  $\text{Ni}_{50}\text{Pt}_{50}$  alloy is in relatively good agreement with the experimental value of 920 K. Surface MC simulations have been carried out in the same temperature range by the direct exchange Monte Carlo (DEMC) method in the grand-canonical ensemble [8,26]. The simulation cell geometry and the relevant parameters of the calculations are the same as used in Ref. [8].

The bulk MC and surface DEMC simulations have been carried out for one stoichiometric ( $\text{Ni}_{50}\text{Pt}_{50}$ ) and two slightly off-stoichiometric ( $\text{Ni}_{49}\text{Pt}_{51}$  and  $\text{Ni}_{51}\text{Pt}_{49}$ ) bulk compositions. The temperature dependence of the Pt concentration in the surface ( $\lambda = 1$ ) and subsurface ( $\lambda = 2$ ) layers in those three cases is displayed in Fig. 1.

First of all one can notice that the first layer is enriched by Pt while the second layer is enriched by Ni. This is just a consequence of the fact that the surface segregation energies of Pt into the first and second layers are  $-705$  and  $231$  K [8], respectively (according to the convention adopted here, a negative value of the segregation energy means that Pt segregates to the corresponding layer, and vice versa, positive values favor Ni segregations). At temperatures above the order-disorder transition,  $T > T_c$ , the Pt concentration in the surface layer and Ni concentration in the second layer decreases with increasing temperature in all three cases, which is the standard Langmuir-McLean behavior.

However, at temperatures below the order-disorder transition,  $T < T_c$ , the composition of the surface layers behaves differently: It is only for the Pt-rich off-stoichiometric alloy,  $\text{Ni}_{49}\text{Pt}_{51}$ , and only in the case of the first layer that the temperature dependence of layer composition follows the same Langmuir-McLean-type of behavior. In all the other cases the so-called endothermic segregation is observed. The reason for the endothermic behavior of the alloy compositions may be understood as follows: the ordering energy, which is approximately 6.5 mRy or 1000 K [8], starts to dominate at low temperatures, thereby pinning the alloy composition in every layer to the corresponding stoichiometric value. From this point of view the surface composition of the  $\text{Ni}_{51}\text{Pt}_{49}$  seems to exhibit a most unusual behavior, and, moreover, the change of segregation occurs sharply with the change of the bulk alloy composition just by 1 at. %.

Such a qualitative transition in the segregation behavior due to a small change of the bulk alloy composition near the stoichiometric value is the so-called off-stoichiometric effect [19] which is connected to the formation of the antisite defects in the alloy due to deviations from the stoichiometric composition. In the

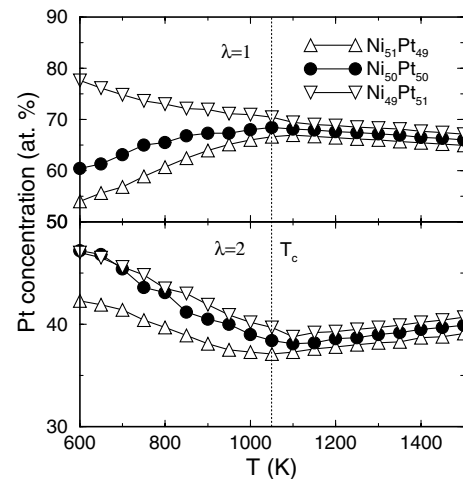


FIG. 1. Composition of the surface ( $\lambda = 1$ ) and subsurface ( $\lambda = 2$ ) layers of the (111) surface in the  $\text{Ni}_{51}\text{Pt}_{49}$  ( $\triangle$ ),  $\text{Ni}_{50}\text{Pt}_{50}$  ( $\bullet$ ), and  $\text{Ni}_{49}\text{Pt}_{50}$  ( $\nabla$ ) alloys versus temperature.

case of Pt-rich off-stoichiometric alloys the excess of Pt atoms should appear on the Ni sublattice, thus an addition of a Pt atom to the alloy leads to the creation of a new partial Pt antisite defect on the Ni sublattice. Such an antisite defect, however, is annihilated, if a Ni atom is added to the alloy. This makes the Pt segregation favorable in the case of Pt-rich off-stoichiometric alloys: It leads to a transfer of Ni atoms from the surface into the bulk and vice versa, Pt atoms from the bulk to the surface, thereby annihilating the partial Pt antisite on the Ni sublattice in the bulk. The segregation of Ni antisite defects in the Ni-rich off-stoichiometric alloys, on the other hand, is largely suppressed due to a general tendency of Pt to segregate toward the surface of NiPt alloys.

The thermodynamics of the off-stoichiometric effect can be understood from a general definition of the surface energy, which for a binary  $A_{1-c}B_c$  alloy can be written as

$$\gamma(\{c_i\}) = F_{\text{surf}}(\{c_i\}) - NF_{\text{bulk}}(c) - \mu \sum_{i=1}^N (c_i - c), \quad (1)$$

where  $\{c_i\}$  is the alloy concentration in layer  $i$ ,  $F_{\text{surf}}$  is the free energy of the surface region (per surface atom),  $F_{\text{bulk}}$  denote the free energy of the bulk (per atom),  $N$  is the number of layers in the surface region,  $c \equiv c_B$  the concentration of the  $B$  component in the bulk, and  $\mu$  is the effective chemical potential. The latter is equal to the difference in the chemical potentials of the two alloy components in the bulk and is given by

$$\mu = \frac{\partial F(c)_{\text{bulk}}}{\partial c}. \quad (2)$$

From Eq. (1) it is clear that the surface alloy composition could be dramatically affected near the stoichiometric composition due to the change of the effective chemical potential. The chemical potential, being a smooth function of the alloy composition in random alloys, abruptly changes near the stoichiometric composition in ordered alloys due to the fact that different atoms create or annihilate partial antisite defects which are different in  $A$ -deficient or  $B$ -deficient off-stoichiometric compositions as has been discussed above. As has been shown in Ref. [19] the chemical potential of an ordered alloy becomes discontinuous at the stoichiometric composition at  $T = 0$ , where actually there exist two different values of the chemical potentials, whose difference is equal to the formation energy of the exchange antisite defect when two different partial antisites are created simultaneously. In the case of  $L1_0$  ordered alloy it is equal to  $8E_{\text{ord}}$ , where  $E_{\text{ord}}$  is the ordering energy, which in NiPt at  $T = 0$  K is about 0.1 Ry. The steplike behavior of the chemical potential becomes, however, smeared out at  $T \neq 0$ , due to the presence of thermal exchange antisite defects, which make possible both the creation and annihilation of the partial antisites when atoms transform between the surface region and the bulk.

In order to investigate the behavior of the effective chemical potential (2) at nonzero temperatures, we have carried out the grand-canonical MC simulation for the bulk NiPt alloys (Fig. 2). In the disordered alloys ( $T = 1400$  K) the effective chemical potential is a linear function of the alloy composition. At temperatures just below the order-disorder phase transition ( $T = 1050$  K) the curve starts to bend at the stoichiometric composition and a smooth step appears at  $T = 600$  K. The only difference from the situation at zero temperature is that no discontinuity in  $\mu$  occurs at the exact stoichiometric concentration. Instead  $\mu$  exhibits a continuous, although quite sharp behavior at low temperatures, increasing in the vicinity of the stoichiometric composition. One can also notice that the size of the step changes with temperature: This is a consequence of the fact that the energy of the exchange antisite defect is proportional to the value of the long-range parameter which increases with decreasing temperature [27].

Finally, in Fig. 3 we show configurations of the first two surface layers of the  $\text{Ni}_{49}\text{Pt}_{51}$  ordered alloy obtained in the DEMC simulations at  $T = 600$  K. One can notice that the subsurface layer ( $\lambda = 2$ ) has a  $2 \times 1$  structure which corresponds to the (111) truncation of the bulk  $L1_0$  ordered structure. At the same time, the Pt-rich surface layer ( $\lambda = 1$ ) has a partially ordered structure: Ni and Pt atoms have a clear long-range order in the direction which corresponds to the ordering of the Ni and Pt rows in the subsurface layer. However, they are to some extent distributed randomly in the other direction. That is, the structure of the surface layer can also be identified as  $p(2 \times 1)$  and at the same time, one clearly sees the patterns of the  $2 \times 2$  structure which corresponds to the structure of the  $L1_2(111)$  surface with  $A_3B$  stoichiometry.

Therefore, the change in the atomic configuration that emerges from our calculations can be partly attributed to the surface induced disorder which takes place for the (111) surface of the  $L1_0$  structure [12] in the system with

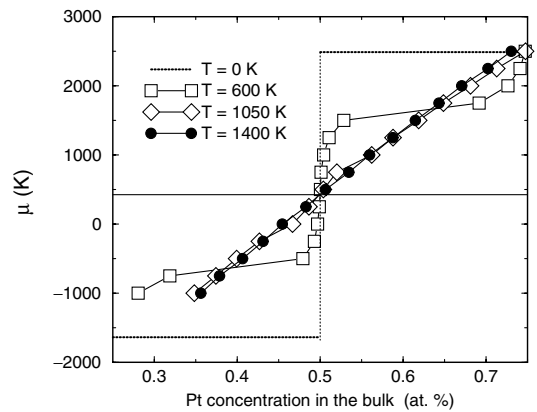


FIG. 2. Concentration dependence of the bulk chemical potential  $\mu$  in fcc Ni-Pt alloy from the grand-canonical Monte Carlo simulations at different temperatures.

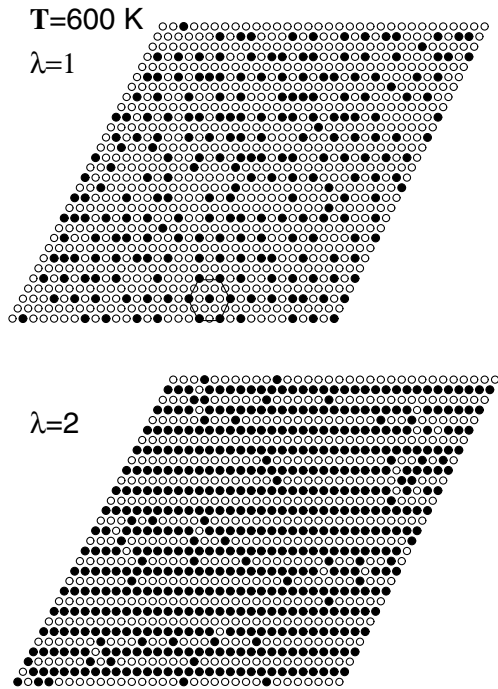


FIG. 3. Simulated structure of the surface ( $\lambda = 1$ ) and sub-surface ( $\lambda = 2$ ) layers at 600 K. ● and ○ designate Ni and Pt atoms, respectively. A pattern of  $2 \times 2$  ordered structure present in most places in the surface layer is indicated by lines.

an ordering type of interactions. In addition it also reflects the existence of a well-determined ground state for the  $A_3B$  alloy on the triangle lattice which is the  $2 \times 2$  structure due to the negative and, thus, segregation-type effective interaction at the forth coordination shell in this system [8].

In summary, concentration profiles of the (111) surface of NiPt alloys around equiatomic concentration have been calculated from first principles and the existence of the off-stoichiometric effect at nonzero temperature is demonstrated from MC simulations. The latter is caused by the abrupt change of the effective chemical potential in the bulk at the stoichiometric composition. At temperatures below the order-disorder transition the unusual behavior of the surface composition and surface structure is observed theoretically. In the stoichiometric and Ni-rich alloys the ordering effects tend to pin the alloy composition in every layer to the corresponding stoichiometric value, leading to a decrease of the Pt segregation with temperature. On the contrary, in Pt-rich ordered alloy surface segregation is calculated to be enhanced compared to the random alloy case. As a consequence, we predict that just 1 at.% change in the bulk Pt concentration may lead to more than 20 at.% change in the Pt concentration at the surface.

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